RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.Sc. THIRD SEMESTER EXAMINATION, DECEMBER 2014

SECOND YEAR

Date : 19/12/2014 **CHEMISTRY (Honours)**

Time : 11 am – 1 pm **Paper :** III (Gr. C) Full Marks : 25

Unit – I

(*Answer **any one** question*) [1×13]

1. a) $E^{o}_{Fe^{+3}/Fe^{+2}} = 0{\cdot}77V$ and $E^{o}_{I_2/2I^-} = 0{\cdot}54$

   Can ferric quantitatively oxidise iodide to iodine? Explain. [2½]

   b) What is 'super acid'? Why it is so named? [1½+2]

   c) Explain red-ox properties of Tl^{+3}/Tl^{+} couple at acidic and alkaline condition. Given $E^{o}_{T\ell^{+3}/T\ell^{+}} = 1{\cdot}28V$ and K_{Sp} of $T\ell(OH)_3 = 1\times10^{-43}$. [3]

   d) Predict the direction of the following reaction. Explain your answer $AgF_2 + 2I^- = AgI_2 + 2F^-$. [2]

   e) Would decrease, increase or have no effect on the acidity or basicity of the solution when zinc amide is added to a liquid ammonia solution of potassium amide and explain by proper acid-base concept. [2]

2. a) What is transition potential? Can iron (II) to be estimated by dichromate using barium diphenyl amine sulphonate indicator. $E^{o}_{Fe^{3+}/Fe^{+2}} = 0{\cdot}77V$ $E^{o}_{Cr_2O_7^{2-}/2Cr^{+3}} = 1{\cdot}33V$; $E^{o}_{Ind(OX)/Ind(Red)} = 0{\cdot}85V$ [2½]

   b) Given the following standard reduction potentials in acidic medium $E^{o}_{(Ce^{4+}/Ce^{3+})} = 1{\cdot}55V$; $E^{o}_{(Fe^{3+}/Fe^{2+})} = 0{\cdot}77V$

   Calculate the potential at the equivalence point of the titration of a 25ml 0·1(N) Fe^{2+} solution by a 0·1 (N) solution of Ce^{4+}. What are the concentrations of the unchanged Fe^{2+} and Ce^{4+} at the equivalence point? [2+2]

   c) What happens when hydrochloric acid is added separately to HgO and HgS. Explain the course of reaction with concerned acid-base concept. [1½]

   d) Construct the Frost diagram for manganese from the following latimer diagram and comment on the stability of Mn^{+3} ion in acidic aqueous solution

   $$MnO_4^- \xrightarrow{0{\cdot}564\,V} MnO_4^{=} \xrightarrow{2{\cdot}26V} MnO_2 \xrightarrow{0{\cdot}95V} Mn^{3+} \xrightarrow{1{\cdot}51V} Mn^{2+} \xrightarrow{-1{\cdot}18V} Mn$$ [3]

   e) Given pK_a's for some oxy acids of phosphorous. H_3PO_4 : 2·1; H_3PO_3 : 1·8; H_3PO_2 : 2; Determine the basicity of the acids. [2]

Unit – II

(*Answer **any one** question*) [1×12]

3. a) Construct the MO energy level diagram of H_2O molecule and hence predict the nature of bonds formed. [2+1]

   b) Explain the flexidentate character of EDTA with example and discuss the effect of pH on it. [3]

   c) A species of composition $CoBr_3$, $2H_2O$, $4NH_3$ shows a molar conductivity 420 $ohm^{-1}cm^2$ at infinite dilution. Suggest the probable formulation. [2]

   d) A rose-red precipitate is formed when $NiSO_4$ is treated with dimethyl glyoxime in presence of ammonia. Give its structure. What will happen if the alkalinity of the solution is raised? [2]

   e) Which one has greater b.p (°C) H_2O or D_2O? Explain. [2]

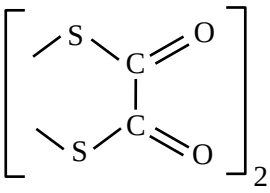
4. a) What are extrinsic semiconductors? How does variation of doping leads to n– or p–type semiconductors. [3]

b) The nitrite ion forms both the complexes $[Co(NH_3)_5(ONO)]^{2+}$ (O-bonded) and $[Co(NH_3)_5(NO_2)]^{2+}$ (N-bonded), but the latter is more stable— Explain. [2]

c) Due to Frenkel defects, the dielectric constant in the ionic crystals increases. Explain [2]

d) Write down the IUPAC names of the following (**<u>any one</u>**) : [1]

i) $K_2[OsCl_5N]$

ii) Pt  2

e) Why Macrocyclic compounds are more stable than normal chelate complexes? [2]

e) Suggest why a chelated complex is more stable than a similar nonchelated complex? [2]

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